Cloud Point and Surface Tension Studies of Triblock Copolymer−Ionic Surfactant Mixed Systems in the Presence of Amino Acids or Dipeptides and Electrolytes

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This paper is focused on the influence of some amino acids or dipeptides (glycine, L-alanine, L-valine, L-threonine, L-proline, glycylglycine, and glycyl-DL-valine) and electrolytes (NaCl, $MgCl_2$, Na_2SO_4, and Na_3PO_4) on the cloud point (CP) and surface properties of pure triblock copolymers [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ and $(EO)_{13}(PO)_{30}(EO)_{13}$ (L-64)] and their mixed systems with cationic surfactants [dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide] and anionic surfactants [sodium dodecylsulphate (SDS), sodium dodecylbenzene sulfonate (SDBS), and dioctyl sulphosuccinate sodium salt (AOT)]. The CP of the mixed system of triblock copolymers and surfactants is more than that of pure triblock copolymers. The decrease in the CP behavior of pure triblock copolymers as well as their mixed systems with ionic surfactants have been explained on the basis of the polar or nonpolar characteristics and the steric factor of the side chains of both amino acids and dipeptides. The variation of the CP of pure triblock copolymers and their mixed systems in the presence of electrolytes has been explained on the basis of salting-in or salting-out nature and the co- and counterion effect, respectively. The effect of amino acids or dipeptides on the surface properties of pure triblock copolymers and their mixed systems with ionic surfactants has been attributed to the hydrophobicity and steric effect of the side chains of these additives.

Introduction

An interesting class of water-soluble block copolymeric amphiphiles is of poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide), PEO−PPO−PEO, triblock copolymers[1−3] marketed under different trade names, namely, Pluronics (BASF), Synperonics (ICI), Epans, and so forth, as flakes, liquids, and pastes. Because of their unique aggregational behavior, Pluronics are extensively used in a variety of applications such as in cosmetics, pharmaceuticals, textile industries,[3] and so forth. The highest degree of surface activity is observed in copolymers with relatively long PPO segments and short PEO segments.[4] On the other hand, longer PEO blocks display superior wetting behavior. Triblock copolymers are more beneficial than conventional neutral polymers because of the presence of both hydrophilic (i.e., PEO) and hydrophobic (i.e., PPO) predominant moieties in the same polymer macromolecule. These polymers also act as nonionic surfactants, since the amphiphilic character of block copolymers leads to self-assembly behavior resembling that of classical nonionic surfactants.

The cloud point (CP) is the temperature above which turbidity or precipitation of an aqueous solution of water-soluble surfactant starts. It is a reversible process and is especially noted with triblock copolymers. When the solutions are heated sufficiently, the hydrophilic PEO chains become dehydrated, and the solubility of the surfactant decreases noticeably. This causes its micelles to coalesce and grow to sizes that are large enough to make the solution turbid. Above the CP, phase separation occurs, and the solution separates into two isotropic phases; one phase is surfactant-rich, and the other is surfactant-poor. This phenomenon is of both practical and theoretical interest, and its practical efficacy lies in the fact that detergency reaches a maximum around the CP.[5−8]

It is well-established that the addition of ionic surfactants increases the CPs of their nonionic counterparts.[9−13] The incorporation of ionic surfactant molecules into the nonionic micelles introduces electrostatic repulsions between the micelles, thus hindering the coacervate phase formation and raising the CP. Valaulikar and Manohar[14] have demonstrated that an increase in the CP can be related to the surface charge per micelle that keeps the micelle apart. This supports the view that micelle coalescence, rather than micellar growth, is responsible for the clouding process. The mixtures of ionic and nonionic surfactants exhibit surface properties significantly better than either of the components alone. In addition, such synergistic effects greatly improve surfactant properties as observed in such mixed micellar systems, leading to their use in detergent applications, separations, and micellar liquid chromatography.[15]

The value of the CP depends on the structure and concentration of the surfactant and the presence of additives.[13,16−19] The analysis of interfacial and thermodynamic properties of surfactants in solutions, both in the presence and in the absence of additives, can provide a wealth of information of solute−solute and solute−solvent interactions of the surfactant in solution. The CP of triblock copolymers can be conveniently decreased or increased in the presence of various additives, thus providing a way to use them under different conditions.

Many proteins interact strongly with amphiphilic molecules, and these interactions are of immense significance to understand the various aspects of life processes and of vast importance in industrial applications.[20,21] Therefore, it is very important to understand the origin and nature of protein−surfactant interac-

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tions both qualitatively and quantitatively. Amino acids are zwitterionic biomolecules and basic structural units of proteins.[22] At present, researchers are showing keen interest in amino acid−surfactant−water systems.[23,24] The interactions between surfactants and amino acids may affect the activity of the latter. These interactions can also influence the micellization process. The side chains of these building blocks differ in size, shape, charge, hydrogen-bonding capacity, hydrophobicity, and chemical reactivity. Individually and collectively, these side chains contribute to the structure and function of proteins.

The aim of this paper is to investigate the effect of amino acids or dipeptides and electrolytes on the CP and surface properties of pure triblock copolymers and their mixed systems with ionic surfactants. The two triblock copolymers (TBP) chosen for the study differ in the number of PEO units.

Experimental Section

Materials. The cationic surfactants, dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide (HTAB), of 0.98 mass fraction purity, the anionic surfactant, dioctyl sulphosuccinate sodium salt (AOT), of 0.96 mass fraction purity, and amino acids (glycine, L-alanine, L-proline, L-threonine, L-valine) and dipeptides (glycylglycine and glycyl-DL-valine), all of 0.99 mass fraction purity, were purchased from Lancaster Synthesis, UK. The two triblock copolymers $(EO)_{13}(PO)_{30}(EO)_{13}$, L64 (MW = 2900) and $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ (MW = 2036) and anionic surfactants such as sodium dodecylsulphate (SDS) and sodium dodecylbenzene sulfonate (SDBS) all of 0.99 mass fraction purity were obtained from Aldrich. The inorganic salts of 0.99 mass fraction purity (NaCl, $MgCl_2$, Na_2SO_4, Na_3PO_4) were obtained from CDH, Mumbai (India), and were of analytical grade. All of the chemicals were used as received. A Sartorius analytical balance with a precision of ± 0.0001 g was used for weighing the amount of different substances. Different solutions were prepared by dissolving accurately weighed quantities in requisite volumes of deionized double-distilled water. All measurements have been performed at 298.15 K after giving overnight time for stabilization.

Apparatus and Procedure. CP Measurements. The values of the CP of various surfactant systems can be obtained either with visual observation or the spectrophotometric method. In the present work, we have employed the visual method for the determination of the CP. In this method, the CP measurements of surfactant solutions were determined by heating them in glass tubes suspended in an oil bath, whose temperature was increased gradually with constant stirring at a rate of about 0.1 $K\cdot min^{-1}$. CPs were determined visually by noting the abrupt change in the appearance of surfactant solution from clear to turbid. The temperature at which turbidity first appeared was recorded. The solution was then allowed to cool slowly, and the temperature at which it became clear again was also recorded. The maximum error in the CP value is 0.5 % calculated from at least three determinations. The results were reproducible within ± 0.5 K. The mass fractions (w) of both triblock copolymers used for measurements were $w = 0.01$, as after $w = 0.01$ the CP becomes almost constant with increasing concentration of the polymer but varies significantly below $w = 0.01$, as is evident from Figure 1.

Surface Tension Measurements. The surface tension values of the systems were measured with a Du Nouy ring tensiometer (Kruss Easy Dyne tensiometer) from Kruss Gmbh (Hamburg, Germany) using a platinum ring at 298.15 K. The measurements were performed at (298.15 ± 0.5) K diluting a concentrated surfactant solution contained in the thermostatted vessel with water. The accuracy in the measurement of surface tension with the tensiometer is ± 0.15 $mN\cdot m^{-1}$.

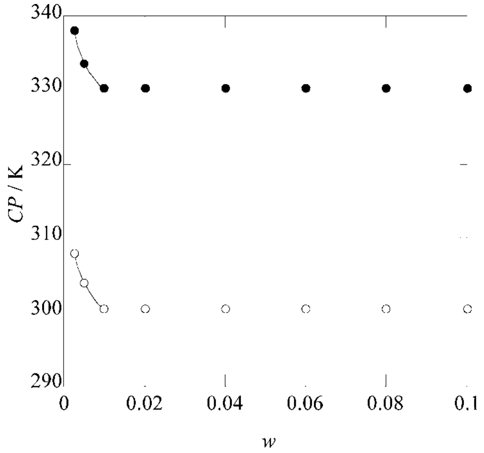

Figure 1. Clouding behavior of aqueous solutions of the two triblock copolymers at different mass fractions, w: ●, $(EO)_{13}(PO)_{30}(EO)_{13}$; ○, $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$.

Table 1. CP of Various Ionic Surfactants + $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$)/$(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$)

system	CP/K
$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$	300.45
$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ + DTAB ($60\cdot10^{-3}$ $mol\cdot dm^{-3}$)	315.15
$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ + TTAB ($30\cdot10^{-3}$ $mol\cdot dm^{-3}$)	346.05
$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ + HTAB ($20\cdot10^{-3}$ $mol\cdot dm^{-3}$)	326.95
$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ + SDS ($20\cdot10^{-3}$ $mol\cdot dm^{-3}$)	329.15
$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ + SDBS ($30\cdot10^{-3}$ $mol\cdot dm^{-3}$)	319.65
$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ + AOT ($10\cdot10^{-3}$ $mol\cdot dm^{-3}$)	319.95
$(EO)_{13}(PO)_{30}(EO)_{13}$	330.25
$(EO)_{13}(PO)_{30}(EO)_{13}$ + DTAB ($2\cdot10^{-3}$ $mol\cdot dm^{-3}$)	348.15
$(EO)_{13}(PO)_{30}(EO)_{13}$ + TTAB ($2\cdot10^{-3}$ $mol\cdot dm^{-3}$)	361.15
$(EO)_{13}(PO)_{30}(EO)_{13}$ + HTAB ($0.5\cdot10^{-3}$ $mol\cdot dm^{-3}$)	350.65
$(EO)_{13}(PO)_{30}(EO)_{13}$ + SDS ($0.5\cdot10^{-3}$ $mol\cdot dm^{-3}$)	344.65
$(EO)_{13}(PO)_{30}(EO)_{13}$ + SDBS ($1\cdot10^{-3}$ $mol\cdot dm^{-3}$)	325.15
$(EO)_{13}(PO)_{30}(EO)_{13}$ + AOT ($0.5\cdot10^{-3}$ $mol\cdot dm^{-3}$)	342.65

Results and Discussion

Figure 1 shows the variation in the CP behavior of the two triblock copolymers as a function of their mass fraction. We observe a small dependence of the CP with varying mass fraction of TBPs. The CP decreases abruptly up to the mass fraction, $w = 0.01$, of TBP, and after that values of CP remain almost constant with a further increase in the mass fraction of TBP. The values of the CP of the two TBPs at $w = 0.01$ are given in Table 1, and they are in close agreement to the literature values.[25]

The addition of both cationic (DTAB, TTAB, and HTAB) as well as anionic (SDS, SDBS, and AOT) surfactants results in a significant increase in the CP of both TBPs (Table 1). It has been reported that for a particular class of nonionic surfactants, the number of ethylene oxide units in the molecule have a dramatic effect on their CP.[26] The ionic monomers are charged, and when they are added to TBP solutions, they form mixed micelles. The mixed micelles formed are also charged and generate electrostatic repulsions between different micelles and make them more hydrophilic. The increase in hydrophilicity brings about an increase in the CP.[18,27] From Table 1 we also find that a lower concentration of ionic surfactants is required to bring about a significant increase in the CP of $(EO)_{13}(PO)_{30}(EO)_{13}$ as compared to the TBP, $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$, where higher concentrations of these surfactants are needed. This is

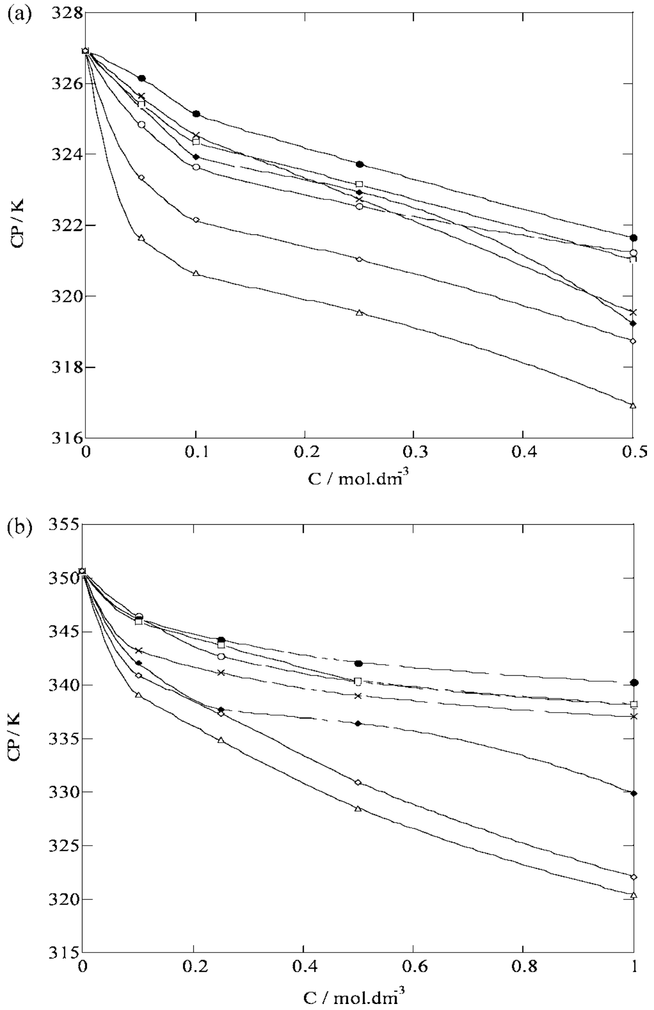

Figure 2. Effect of concentration, *C*, of the amino acids on the CP of mixed systems (a) $[(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + HTAB ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) $[(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + HTAB ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]: ○, glycine; ●, L-alanine; ♦, L-proline; ×, L-threonine; □, L-valine; △, glycyl-DL-valine; ◊, glycylglycine.

because $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ does not show ideal mixed micelle formation with conventional surfactants due to a high PPO/PEO ratio, but it does show mixed micelle formation to some extent which results in an increase in the CP. The results further indicate that for the cationic surfactants under study, the amount of HTAB required to bring about an observable increase in CP is less than TTAB which in turn is less than DTAB. This is because HTAB has a larger hydrophobic carbon chain than TTAB and DTAB. It was found that the ionic surfactants interact more strongly with $(EO)_{13}(PO)_{30}(EO)_{13}$ as compared to $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$.

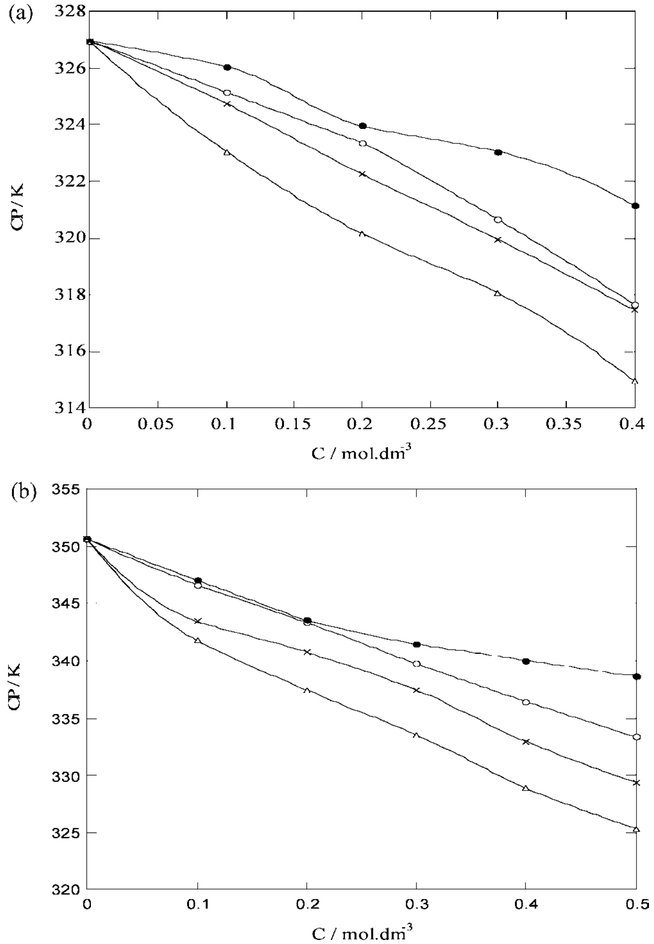

Figure 3. Effect of concentration, *C*, of electrolytes on the CP of mixed systems (a) $[(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + HTAB ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) $[(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + HTAB ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]: ○, NaCl; ●, $MgCl_2$; □, Na_2SO_4; △, Na_3PO_4.

Influence of Amino Acids or Dipeptides on the CP of Various Surfactant Systems. Amino acids have common hydrophilic head groups ($-COOH$, $-NH_2$) and various different hydrophobic side chains and to an extent exhibit surface activity. The association between them and surfactants include electrostatic and hydrophobic interactions. They are also considered to be strong structure-breakers in aqueous solution because of the presence of peripheral charges and generally undergo strong electrostatic interactions with charged species in aqueous solution. From our results, we find that all of the amino acids and dipeptide additives decrease the CP of pure TBPs and mixed systems [TBP + ionic surfactant]. Figure 2 shows the decrease in the CP of the mixed system [TBPs + HTAB] in the presence of various amino acids or dipeptides. Similar results were obtained with other mixed systems (figures not shown). Tables 2 to 4 show the effect of these additives on the CP of pure TBPs and their mixed systems [TBPs + HTAB] and [TBPs + SDS], respectively. The effect can be explained by taking into account the polar or nonpolar characteristics and steric effects of the side chains of amino acids or dipeptides. All of the amino acids used in our work are nonpolar and neutral with the exception of threonine, which is polar and neutral. The addition of nonpolar and uncharged polar amino acids causes a decrease in the CP of all of the systems. The amino acids used, to some extent, prefer a polar environment, and thus they would partition in the headgroup region. This partitioning would replace the amount of water near the headgroup region with a lower temperature to obtain the CP phenomenon, and these nonpolar and uncharged polar amino acids produce decreasing effects on the CP of TBPs and their mixed system with the ionic surfactant. The decrease of the CP of the two TBPs and their mixed systems with ionic surfactants by the amino acid or dipeptide additives follows the order: L-alanine < glycine < L-valine < L-threonine < L-proline < glycylglycine < glycyl-DL-valine. L-Alanine prefers the polar environment to a lesser extent than glycine, and thus glycine produces more depression in CP than L-alanine. The other amino acids, L-valine, L-threonine, and L-proline are more hydrophobic than glycine and L-alanine, and therefore the CP depression is more in them. In the case of L-proline, since the steric effect is more due to the presence of pyrrolidine ring, it depresses the CP to a greater extent than

Table 2. Effect of Concentration, *C*, of Amino Acids or Dipeptides on the CP of (a) $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ (w = 0.01) and (b) $(EO)_{13}(PO)_{30}(EO)_{13}$ (w = 0.01)

	CP/K													
C	glycine		L-alanine		L-proline		L-threonine		L-valine		glycyl-DL-valine		glycylglycine	
$mol \cdot dm^{-3}$	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	300.45	330.25	300.45	330.25	300.45	330.25	300.45	330.25	300.45	330.25	300.45	330.25	300.45	330.25
0.05	299.75	322.25	299.35	323.05	299.55	320.35	299.45	320.55	299.25	321.75	298.85	319.65	299.05	320.95
0.10	298.55	319.75	298.35	321.65	298.05	318.25	298.15	317.45	298.35	318.45	297.75	317.45	297.15	317.95
0.25	297.25	317.45	297.25	320.35	296.55	314.35	297.05	315.35	297.15	316.75	295.95	313.45	295.65	314.85
0.50	295.25	315.35	296.05	316.35	294.35	311.85	294.55	312.35	294.95	314.25	293.05	310.05	293.25	310.65

Table 3. Effect of Concentration, *C*, of Amino Acids or Dipeptides on the CP of Mixed Systems (a) [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ (w = 0.01) + HTAB ($20 \cdot 10^{-3}$ $mol \cdot dm^{-3}$)] and (b) [$(EO)_{13}(PO)_{30}(EO)_{13}$ (w = 0.01) + HTAB ($0.50 \cdot 10^{-3}$ $mol \cdot dm^{-3}$)]

	CP/K													
C	glycine		L-alanine		L-proline		L-threonine		L-valine		glycyl-DL-valine		glycylglycine	
$mol \cdot dm^{-3}$	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	326.95	350.65	326.95	350.65	326.95	350.65	326.95	350.65	326.95	350.65	326.95	350.65	326.95	350.65
0.05	324.85	346.45	326.15	346.25	325.35	342.05	325.65	343.25	325.45	345.95	321.65	339.15	323.35	340.95
0.10	323.65	342.75	325.15	344.25	323.95	337.75	324.55	341.15	342.35	343.75	320.65	334.85	322.15	337.35
0.25	322.55	340.35	323.75	342.15	322.95	336.45	322.75	339.05	323.15	340.45	319.55	328.55	321.05	330.95
0.50	321.25	338.15	321.65	340.25	319.25	329.95	319.55	337.05	321.05	338.25	316.95	320.45	318.75	322.15

Table 4. Effect of Concentration, *C*, of Amino Acids or Dipeptides on the CP of Mixed Systems (a) [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ (w = 0.01) + SDS ($20 \cdot 10^{-3}$ $mol \cdot dm^{-3}$)] and (b) [$(EO)_{13}(PO)_{30}(EO)_{13}$ (w = 0.01) + SDS ($0.50 \cdot 10^{-3}$ $mol \cdot dm^{-3}$)]

	CP/K													
C	glycine		L-alanine		L-proline		L-threonine		L-valine		glycyl-DL-valine		glycylglycine	
$mol \cdot dm^{-3}$	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	329.15	345.65	329.15	345.65	329.15	345.65	329.15	345.65	329.15	345.65	329.15	345.65	329.15	345.65
0.05	327.75	343.95	327.95	343.65	326.05	342.85	327.45	343.45	327.35	343.65	325.25	342.65	326.25	342.95
0.10	326.95	342.05	326.75	342.25	324.65	339.35	325.45	342.15	325.45	341.85	323.55	339.35	324.55	340.75
0.25	325.25	340.25	325.65	341.45	322.55	338.25	323.15	340.25	323.75	340.55	321.25	337.95	322.45	338.95
0.50	323.45	339.15	324.55	340.45	321.15	337.35	321.75	338.45	328.15	338.95	319.55	335.65	320.75	337.05

Table 5. Effect of Concentration, *C*, of Electrolytes on the CP of (a) $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ (w = 0.01) and (b) $(EO)_{13}(PO)_{30}(EO)_{13}$ (w = 0.01)

	CP/K							
C	NaCl		$MgCl_2$		Na_2SO_4		Na_3PO_4	
$mol \cdot dm^{-3}$	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	300.45	330.25	300.45	330.25	300.45	330.25	300.45	330.25
0.10	299.35	327.75	299.95	328.05	299.35	323.25	297.65	321.85
0.20	296.55	324.75	297.85	325.15	296.85	319.15	294.75	315.85
0.30	294.15	321.75	296.75	322.55	293.55	315.95	292.65	313.95
0.40	291.15	318.85	294.85	320.65	290.75	312.75	289.55	311.15
0.50		314.55		319.85		309.35		305.35

Table 6. Effect of Concentration, *C*, of Electrolytes on the CP of Mixed Systems (a) [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ (w = 0.01) + HTAB ($20 \cdot 10^{-3}$ $mol \cdot dm^{-3}$)] and (b) [$(EO)_{13}(PO)_{30}(EO)_{13}$ (w = 0.01) + HTAB ($0.50 \cdot 10^{-3}$ $mol \cdot dm^{-3}$)]

	CP/K							
C	NaCl		$MgCl_2$		Na_2SO_4		Na_3PO_4	
$mol \cdot dm^{-3}$	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	326.95	350.65	326.95	350.65	326.95	350.65	326.95	350.65
0.10	325.15	346.65	326.05	347.05	324.75	343.45	323.05	341.75
0.20	323.35	343.35	323.95	343.55	322.25	340.75	320.15	337.45
0.30	320.65	339.75	323.05	341.45	319.95	337.45	318.05	333.55
0.40	317.65	336.45	321.15	340.05	317.45	332.95	314.95	328.85
0.50		333.35		338.65		329.35		325.35

L-valine and L-threonine. Among the dipeptides used, the glycyl-DL-valine depresses the CP of the various systems to a greater extent than glycylglycine. This is due to the greater hydrophobicity or steric factor in the case of glycyl-DL-valine. It is observed that dipeptides decrease the CP more than the constituent amino acids. The results were similar with other systems [TBPs $(EO)_{13}(PO)_{30}(EO)_{13}$/$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ + DTAB/TTAB/SDBS/AOT] (tables not shown).

Influence of Electrolytes on the CP of Various Surfactant Systems. Table 5 shows the effect of electrolytes NaCl, $MgCl_2$, Na_2SO_4, and Na_3PO_4 on the CP of the two TBPs. Figure 3 shows the decrease of the CP of the mixed system [TBPs + HTAB] in the presence of various electrolytes. Similar behavior was obtained with other systems (figures not shown). Similarly, Tables 6 and 7 show the effect of these electrolytes on the CP of the mixed systems [TBPs + HTAB] and [TBPs + SDS], respectively. In all of the cases, it is observed that the electrolytes decrease the CP by promoting the dehydration of PEO chains. The effect of electrolytes on the CP of two TBPs and their mixed systems with ionic surfactants is explained on the basis of their salting-in or out nature. Anions, which are strong water-structure formers[28] and increase the hydrogen bonding among water molecules, decrease the hydration of the ether groups of the surfactant, reducing its solubility, salting it out, and thus lowering its CP. The added salts provide additional counterions to the existing systems and enhance counterion binding; as a result, the water of hydration is removed from the headgroup region, resulting in a decrease of their CP. The SO_4^{2-} and PO_4^{3-} ions are also known as water-structure formers; hence, Na_2SO_4 and Na_3PO_4 should have a more pronounced effect in decreasing the CP of the various systems. This is indeed observed, and the order of CP depression is found to be $Na_3PO_4 > Na_2SO_4 > NaCl$. Also, we find that $MgCl_2$ causes less depression in the CP than NaCl as observed in Tables 5 to 7. This is because divalent cations form complexes with the ether linkage of TBPs, thus increasing their solubility in water and raising their CP. Similar results were obtained with other systems [TBPs + ionic surfactant] (tables not shown).

Table 7. Effect of Concentration, *C*, of Electrolytes on the CP of Mixed Systems (a) $[(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + SDS ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) $[(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + SDS ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]

	CP/K							
C	NaCl		MgCl$_2$		Na$_2$SO$_4$		Na$_3$PO$_4$	
mol·dm^{-3}	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	329.15	344.65	329.15	344.65	329.15	344.65	329.15	344.65
0.10	327.75	341.75	328.35	342.15	327.85	337.65	326.05	335.85
0.20	324.95	338.95	326.15	339.25	325.35	333.85	323.25	330.45
0.30	322.65	334.55	325.05	336.85	323.15	329.35	321.15	326.05
0.40	319.75	331.25	323.25	335.05	321.65	326.25	318.05	324.05
0.50		328.35		333.85		323.75		319.55

Table 8. Effect of Concentration, *C*, of Amino Acids or Dipeptides on the Surface Tension, γ, of (a) $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) and (b) $(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$)

	γ/mN·m^{-1}													
C	glycine		L-alanine		L-proline		L-threonine		L-valine		glycyl-DL-valine		glycylglycine	
mol·dm^{-3}	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	39.3	41.5	39.3	41.5	39.3	41.5	39.3	41.5	39.3	41.5	39.3	41.5	39.3	41.5
0.10	38.9	40.6	39.0	40.8	38.4	40.0	38.5	40.2	38.7	40.4	38.1	39.7	38.2	39.9
0.25	38.5	39.8	38.7	40.0	38.0	39.0	38.1	39.2	38.2	39.3	37.9	38.9	37.8	39.1
0.50	38.1	38.8	38.3	39.0	37.5	38.3	37.7	38.4	37.9	38.6	37.1	37.8	37.4	38.0
1.00	37.7	38.1	38.0	38.7	37.2	37.1	37.3	37.3	37.6	37.8	36.8	36.9	37.0	37.1

Table 9. Effect of Concentration, *C*, of Amino Acids or Dipeptides on the Surface Tension, γ, of Mixed Systems (a) $[(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + HTAB ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) $[(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + HTAB ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]

	γ/mN·m^{-1}													
C	glycine		L-alanine		L-proline		L-threonine		L-valine		glycyl-DL-valine		glycylglycine	
mol·dm^{-3}	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	36.7	39.9	36.7	39.9	36.7	39.9	36.7	39.9	36.7	39.9	36.7	39.9	36.7	39.9
0.10	36.5	39.3	36.6	39.5	36.2	38.8	36.4	38.9	36.5	39.1	36.2	38.3	36.4	38.5
0.25	36.3	38.8	36.4	39.0	36.0	38.2	36.2	38.4	36.2	38.6	35.7	37.9	36.1	38.0
0.50	36.1	38.0	36.2	38.4	35.8	37.1	35.9	37.5	36.0	37.6	35.4	36.9	35.7	36.9
1.00	35.9	37.2	36.0	37.5	35.5	36.3	35.7	36.5	35.8	36.9	35.2	35.8	35.4	36.0

Table 10. Effect of Concentration, *C*, of Amino Acids or Dipeptides on the Surface Tension, γ, of Mixed Systems (a) $[(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + SDS ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) $[(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + SDS ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]

	γ/mN·m^{-1}													
C	glycine		L-alanine		L-proline		L-threonine		L-valine		glycyl-DL-valine		glycylglycine	
mol·dm^{-3}	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	39.9	38.9	39.9	38.9	39.9	38.9	39.9	38.9	39.9	38.9	39.9	38.9	39.9	38.9
0.10	39.4	38.0	39.6	38.6	39.0	37.7	39.1	37.9	39.3	38.6	38.6	38.3	38.8	38.5
0.25	39.2	37.8	39.3	38.4	38.8	37.5	38.9	37.7	39.1	37.9	38.2	37.5	38.5	37.9
0.50	39.0	37.5	39.1	37.8	38.6	37.1	38.7	37.4	38.8	37.3	37.9	36.8	38.0	37.0
1.00	38.8	37.3	38.9	37.4	38.4	36.8	38.5	37.0	38.6	37.1	37.5	36.3	37.8	36.5

Table 11. Effect of Concentration, *C*, of Electrolytes on the Surface Tension, γ, of (a) $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) and (b) $(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$)

	γ/mN·m^{-1}							
C	NaCl		MgCl$_2$		Na$_2$SO$_4$		Na$_3$PO$_4$	
mol·dm^{-3}	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	39.3	41.5	39.3	41.5	39.3	41.5	39.3	41.5
0.10	39.1	41.0	39.1	41.1	38.9	39.9	38.8	39.7
0.20	38.8	40.5	38.9	40.7	38.6	39.1	38.4	39.0
0.30	38.6	40.0	38.7	40.3	38.1	38.5	38.0	38.1
0.40	38.4	38.7	38.5	39.0	37.8	37.3	37.4	37.0
0.50		38.4		38.7		36.5		36.2

Influence of the Additives on the Surface Tension Behavior of Various Surfactant Systems. From Tables 8 to 13, it is observed that the addition of amino acids or dipeptides and electrolytes decrease the surface tension values because of the enhancement of surface activity. Since the amino acids are water-structure breaking agents, they decrease the solubility of the hydrocarbon tails of the surfactant as well as increase the interfacial tension among the micelle, hydrophobic core, and aqueous solvent and decrease the surface tension values. The decrease in surface tension of the pure triblock copolymers and their mixed systems with ionic surfactants becomes greater as the concentration of particular amino acids or dipeptides increases. Tables 8 to 13 also show that the decrease in surface tension for all of the systems studied in the presence of amino acids or dipeptides follows the order: L-alanine < glycine < L-valine < L-threonine < L-proline < glycylglycine < glycyl-DL-valine. This order can be explained on the basis of two factors such as hydrophobicity and the steric effect of amino acids or dipeptides. In the case of L-alanine, both factors are stronger than that of glycine, but the steric effect is predominant during

Table 12. Effect of Concentration, C, of Electrolytes on the Surface Tension, γ, of Mixed Systems (a) [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + HTAB ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) [$(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + HTAB ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]

C	γ/mN·m^{-1}							
	NaCl		$MgCl_2$		Na_2SO_4		Na_3PO_4	
mol·dm^{-3}	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	36.7	39.9	36.7	39.9	36.7	39.9	36.7	39.9
0.10	36.2	39.0	36.4	39.1	36.0	38.8	36.1	38.6
0.20	35.8	38.1	35.9	38.3	35.3	38.0	35.0	37.9
0.30	35.1	37.6	35.2	37.8	34.8	36.9	34.4	36.5
0.40	34.8	37.0	34.9	37.3	34.3	35.9	33.9	35.2
0.50		36.6		36.8		35.0		34.0

Table 13. Effect of Concentration, C, of Electrolytes on the Surface Tension, γ, of Mixed Systems (a) [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + SDS ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) [$(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + SDS ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]

C	γ/mN·m^{-1}							
	NaCl		$MgCl_2$		Na_2SO_4		Na_3PO_4	
mol·dm^{-3}	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.00	39.9	38.9	39.9	38.9	39.9	38.9	39.9	38.9
0.10	39.2	38.2	39.3	38.4	39.1	38.1	39.0	37.9
0.20	38.0	36.9	38.1	37.0	37.8	36.6	37.6	36.5
0.30	37.1	35.9	37.4	36.1	35.6	35.9	35.4	35.8
0.40	36.2	35.1	36.5	35.3	35.2	34.7	34.1	34.5
0.50		34.6		34.7		34.4		33.8

interactions with all of the surfactants, resulting in a lesser decrease of surface tension as compared to glycine. In the case of L-valine, the hydrophobicity is dominant over the steric effect, resulting in a greater decrease of surface tension than glycine and L-alanine. L-Proline has a pyrrolidine ring, and thus it displays a greater decrease in surface tension than L-threonine. Among the dipeptides, glycyl-DL-valine has a larger hydrophobicity than glycylglycine and thus decreases the surface tension to a greater extent. Similarly, the other systems [triblock copolymers + ionic surfactant] show the same results (tables not shown).

Thermodynamics. The associated standard Gibbs free energy of the phase separation, ΔG, at the point of clouding is obtained from the standard relation:

$$\Delta G = RT \ln X_c$$

where X_c is the mole fraction of the triblock copolymer in the solution, R is a constant having the value 8.314 J·K^{-1}, and T is the CP temperature in Kelvin scale.

The Gibbs free energy change, ΔG, is negative for all of the systems. The system becomes exothermic with the increase in the hydrophobicity of the system, while being endothermic when there is a decrease in hydrophobicity. In the clouding process, dehydration of polyoxyethylene centers initially takes place with the absorption of heat followed by the association of dehydrated molecules involving the release of heat. The dehydration process contributes less than the association process to produce negative ΔG. Other associated processes like orientation, change in configuration, interfacial adsorption, and so forth, also can contribute to the observed ΔG value. The ΔG values are negative and varied in narrow range as shown in Tables 14 to 16. Similar kinds of values were obtained with other systems (tables not shown). It is also

Table 14. Effect of Concentration, C, of Amino Acids or Dipeptides on the ΔG Values (kJ·mol^{-1}) of (a) $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) and (b) $(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$)

	ΔG/kJ·mol^{-1}							
	0.05 mol·dm^{-3}		0.10 mol·dm^{-3}		0.25 mol·dm^{-3}		0.50 mol·dm^{-3}	
additive	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
glycine	−23.260	−25.907	−23.150	−25.698	−23.027	−25.490	−22.836	−25.283
L-alanine	−23.215	−25.970	−23.129	−25.847	−23.017	−25.714	−22.878	−25.360
L-proline	−23.227	−25.749	−23.099	−25.567	−22.946	−25.214	−22.713	−24.948
L-threonine	−23.219	−25.764	−23.106	−25.502	−22.982	−25.292	−22.724	−24.983
L-valine	−23.204	−25.861	−23.122	−25.599	−22.991	−25.406	−22.757	−25.137
glycylglycine	−23.187	−25.795	−23.025	−25.539	−22.865	−25.243	−22.606	−24.829
glycyl-DL-valine	−23.166	−25.685	−23.061	−25.487	−22.861	−25.102	−22.535	−24.722

Table 15. Effect of Concentration, C, of Amino Acids or Dipeptides on the ΔG Values (kJ·mol^{-1}) of Mixed Systems (a) [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + HTAB ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) [$(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + HTAB ($0.50 \cdot 10^{-3}$ mol·dm^{-3})]

	ΔG/kJ·mol^{-1}							
	0.05 mol·dm^{-3}		0.10 mol·dm^{-3}		0.25 mol·dm^{-3}		0.50 mol·dm^{-3}	
additive	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
glycine	−25.177	−27.853	−25.076	−27.547	−24.967	−27.330	−24.827	−27.111
L-alanine	−25.276	−27.835	−25.188	−27.664	−25.050	−27.464	−24.838	−27.254
L-proline	−25.210	−27.494	−25.088	−27.134	−24.970	−26.988	−24.616	−26.396
L-threonine	−25.233	−27.590	−25.134	−27.406	−24.952	−27.145	−24.634	−26.959
L-valine	−25.218	−27.807	−25.119	−27.616	−24.984	−27.307	−24.752	−27.058
glycylglycine	−25.053	−27.403	−24.944	−27.097	−24.811	−26.534	−24.553	−25.748
glycyl-DL-valine	−24.915	−27.252	−24.816	−26.884	−24.666	−26.270	−24.354	−25.551

Table 16. Effect of Concentration, C, of Amino Acids or Dipeptides on the ΔG Values (kJ·mol^{-1}) of Mixed Systems (a) [$(EO)_{2.5}(PO)_{31}(EO)_{2.5}$ ($w = 0.01$) + SDS ($20 \cdot 10^{-3}$ mol·dm^{-3})] and (b) [$(EO)_{13}(PO)_{30}(EO)_{13}$ ($w = 0.01$) + SDS ($0.50 \cdot 10^{-3/}$ mol·dm^{-3})]

	ΔG/kJ·mol^{-1}							
	0.05 mol·dm^{-3}		0.10 mol·dm^{-3}		0.25 mol·dm^{-3}		0.50 mol·dm^{-3}	
additive	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
glycine	−25.406	−27.653	−25.336	−27.492	−25.181	−27.322	−25.011	−27.192
L-alanine	−25.420	−27.642	−25.317	−27.504	−25.202	−27.408	−25.067	−27.276
L-proline	−25.269	−27.558	−25.147	−27.263	−24.944	−27.132	−24.767	−26.898
L-threonine	−25.377	−27.606	−25.222	−27.487	−24.987	−27.290	−24.808	−27.071
L-valine	−25.369	−27.622	−25.208	−27.471	−25.035	−27.315	−24.841	−27.114
glycylglycine	−25.280	−27.564	−25.134	−27.371	−24.924	−27.176	−24.712	−26.939
glycyl-DL-valine	−25.199	−27.534	−25.045	−27.246	−24.802	−27.049	−24.558	−26.764

observed that Δ*G* values are negative in the presence of additives like amino acids or dipeptides and electrolytes because the amino acid effects on water structure decrease the micellization. Hence, in the presence of amino acids, the surfactant-free water ratio will be more, and hence the micelle formation will be at lower concentration: a relatively more spontaneous process.

Conclusions

Amino acids are the basic structural units of proteins and also means of intermolecular interaction. Some of them are also employed as components of drugs. So, the effects of amino acids on the CP of pure triblock copolymer as well as their mixed systems with ionic surfactants are studied in this paper. The CPs of the mixed systems [triblock copolymer + cationic surfactants] and [triblock copolymer + anionic surfactant] are significantly higher than that of the pure triblock copolymer because of the presence of charge in the micelles of the mixed systems. It was observed that ionic surfactants interact more strongly with $(EO)_{13}(PO)_{30}(EO)_{13}$ as compared to the triblock copolymer $(EO)_{2.5}(PO)_{31}(EO)_{2.5}$. This is due to the high PPO/PEO ratio in the latter. The effect of amino acids or dipeptides and electrolytes on the CP of two triblock copolymers and their mixed systems with ionic surfactants show that both kinds of additives decrease the CP of all of the systems under investigation. Amino acids decrease the CP of all of the systems in the following order: L-alanine < glycine < L-valine < L-threonine < L-proline < glycylglycine < glycyl-DL-valine. This effect is explained on the basis of polar or nonpolar characteristics and steric effects of their side chains. Electrolytes decrease the CP of all of the systems in the following order: $Na_3PO_4 > Na_2SO_4 > NaCl$ and $NaCl > MgCl_2$. This is mainly due to their salting-out/salting-in nature. The surface tension values of all of the systems in the presence of various amino acids or dipeptides follow this order: L-alanine < glycine < L-valine < L-threonine < L-proline < glycylglycine < glycyl-DL-valine. In the presence of electrolytes, the surface tension values decrease in the same order: $Na_3PO_4 > Na_2SO_4 > NaCl$ and $NaCl > MgCl_2$. The Gibbs free energy change, Δ*G*, is negative for all of the systems which show the spontaneity of the clouding phenomenon.

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